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Molecular modelling of chemical sensors based on silica surfaces

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Abstract

Molecular simulations of silica based sensors interacting with explosive molecules in the presence of humidity are reported. In order to investigate how surface details affect sensing performance, three models of silica are obtained by tuning the number of various functional groups present at their surface to make them consistent with available data. These models are validated against experimental nitrogen isotherms. The number of water molecules to be introduced in the system in order to mimic a given value of relative humidity is established. Finally, preliminary simulations of 2,4,6-trinitrotoluene (TNT) molecules interacting with wet surfaces show that TNT molecules lie parallel to the surface while interacting strongly with the hydroxyl group of the silanol.

Keywords: Molecular dynamics (MD) simulations; silica surfaces; explosive molecules; adsorption isotherms; relative humidity

1. Introduction

Due to the increasing use of explosives by terrorists, portable gas sensors are being developed in view of detecting small concentrations of their vapors in the atmosphere [1-2]. The sensing ability of such devices relies on the nature and properties of sensitive coatings which directly interact with surrounding vapours. For instance, the performances of amorphous silica depend on the availability of silanols on their surfaces, which supposedly interact with incoming gaseous molecules. As a result, they are sensitive to humidity as silanols are requested by water molecules. To overcome this problem, silica surfaces

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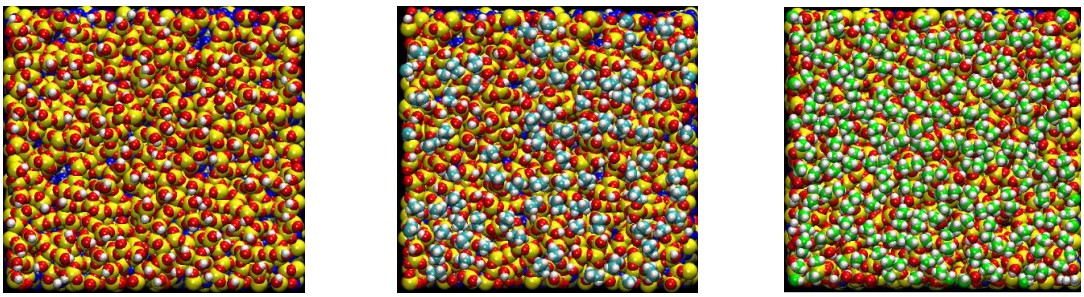
exhibiting hydrophobic methyl groups in addition to silanols may be employed. As a sensing material, amorphous silica exhibits the following advantages: 1) sol-gel synthesis allows the preparation of mesoporous coatings with high specific surface; 2) in view of their high reactivity and versatility, silica surfaces are relatively easy to modify according to the compound to be detected.

Nevertheless, given the variety of explosive molecules, much work is needed to identify suitable surface modifications for every new target. In this context, molecular modelling techniques [3] might be very helpful [4]. However, their ability to provide reliable estimates of sensing responses for sensors based on functionalized silica surfaces is yet to be demonstrated. Required ingredients include interatomic potentials describing silica surface and molecular targets on the same footings, realistic atomistic models of the surfaces, and efficient procedures to estimate the number of adsorbed molecules. The present article provides an overview of work in progress along these lines, whose aim is to simulate 2,4,6-trinitrotoluene (TNT) vapors in the vicinity of silica surfaces and in the presence of humidity. The atomistic models developed are shown to be consistent with N_2 adsorption data. The water molecules at the silica surfaces are quantified depending on ambient humidity. Finally, the preferential interactions of the explosive molecules are characterized. For comparison purpose, three models of silica surfaces are prepared. The Silica-OH surface represents a fully hydroxylated amorphous silica and exhibits only silanols groups at the surface. The two others represent mesoporous silica surfaces synthesized using respectively tetraethoxysilane (TEOS) and dimethoxysilane (DMES) as precursors: Silica-OEt/OH exhibits a mixture of –OH and ethoxy groups, while Silica-$Si(CH_3)_2$/OH exhibits a mixture of hydroxyls and –$Si(CH_3)_2$ groups. The concentration of each group is tuned so that to match the experimental spectroscopic data or litterature available on these surfaces.

2. Computational methods

The present work starts from 3D-periodical models for bulk amorphous silica prepared from heated up α-quartz. These models are extended and cut out so as to obtain two roughly planar surfaces in the 3D-periodic unit cell. Specific algorithms are used to adjust the number of the different surface groups in order to make then consistent with experimental data at hand, while ensuring charge neutrality and a realistic chemical environment for every atom. The surfaces are then equilibrated, either in vacuum or in contact with a vapor, using molecular dynamic (MD) simulations. To obtain adsorption isotherms, molecules in the vicinity of the surfaces are simulated at temperatures above their boiling points and up to the nanosecond time scale to get a vapor phase in equilibrium with adsorbed molecules. The relative humidity (RH) is obtained at temperature T as the ratio of the partial water vapor pressure $P_{vap/H2O}(T)$ to the saturated water vapor pressure $P_{sat/H2O}(T)$. These pressures are calculated from the simulated vapor densities using the ideal gas law. All steps are performed using the gmq package [5].



Silica-OH Silica-OEt/OH Silica-$Si(CH_3)_2OH$

Fig. 1. Structures of present models of silica surfaces : Si=yellow, O=red, H=white, C(Ethoxy)=cyan, C(Methyl)=green.

3. Silica models and corresponding N_2 adsorption isotherms

Following earlier work [6], a hybrid model is used for silica, with an ionic core covered with atoms involved in covalent interactions, including Si and O atoms close to the surface, as well as H and C atoms from silanol, ethoxy and methyl groups. Standard potentials are used for nitrogen and water [7-8], and a new potential has been developed for TNT. Full details will be provided elsewhere.

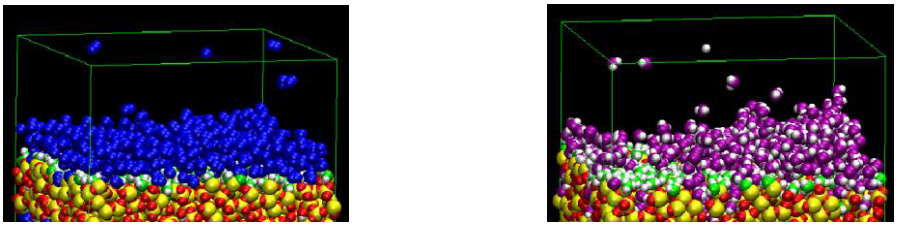


Fig. 2. (a) N_2 (blue) and H_2O (O=purple) molecules at the methylated silica surface at 77K and 453K respectively.

The equilibrated Silica-OH, Silica-OEt/OH and Silica-Si$(CH_3)_2$/OH surfaces are illustrated on Fig.1. They are homogeneously covered with functional groups, with every atom embedded in a reasonable chemical environment. No surprisingly, as such surfaces are put into contact with a vapor phases, most molecules get adsorbed, as illustrated on Fig.2 for N_2 and water. To simulate N_2 adsorption isotherms, each surface is put in contact with an increasing number of N_2 gas molecules and allowed to simulate for at least 1 ns at 77K. N_2 molecules cover the whole surface in a homogeneous way, as shown on Fig.2a. Simulated isotherms are compared to experimental ones measured on mesoporous silica on Fig.3a. Clearly, the capillary condensation of N_2 observed at high pressure cannot be reproduced with our flat surfaces models. Focusing on the linear regime, a good agreement with experiment is obtained. However, the chemical surface groups have no significant influence, in line with the fact that N_2 molecules do not strongly interact with any surface.

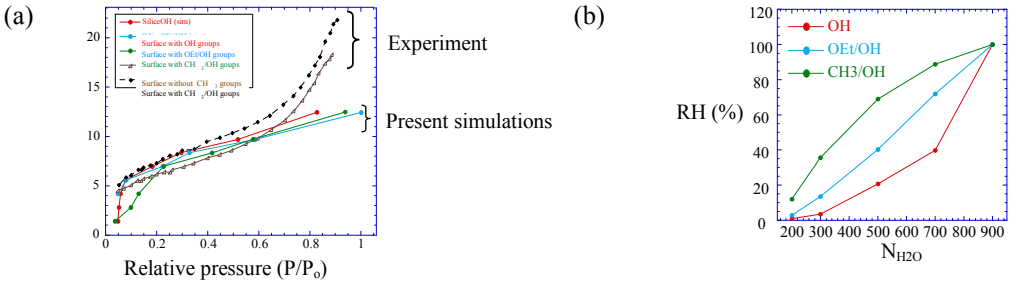


Fig. 3. (a) Simulated N_2 adsorption isotherms at 77K for the silica surfaces compared to experiment [9]; (b) Relative humidity at 453K as a function of the number of water molecules in the simulation box for silica surfaces with water at 453K.

Unlike nitrogen, water molecules strongly interact with silica. As a result, temperatures well above the boiling point of 100°C are required for the adsorption/desorption equilibria to be within the reach of MD simulations. The mass uptake under ambient conditions must therefore be extrapolated from high temperature results. Fig.2b shows that in contrast to nitrogen, water molecules form clusters. This stems from their tendency to avoid methyls. Fig.3b shows RH data for five values of the total number N_{H2O} of water molecules introduced in the simulation box. As expected, RH increases as more hydrophobic silica surfaces are considered because a more significant fraction of N_{H2O} corresponds to gaseous molecules.

4. Interaction of an explosive molecule with a wet methylated surface

Wet methylated Silica-Si$(CH_3)_2$OH surfaces are put in contact with TNT vapor at room temperature. Fig.4 suggests that TNT preferentially interact with silanols, as observed for dry surfaces, although hydrogen bonding may also occur between nitro groups and water molecules.

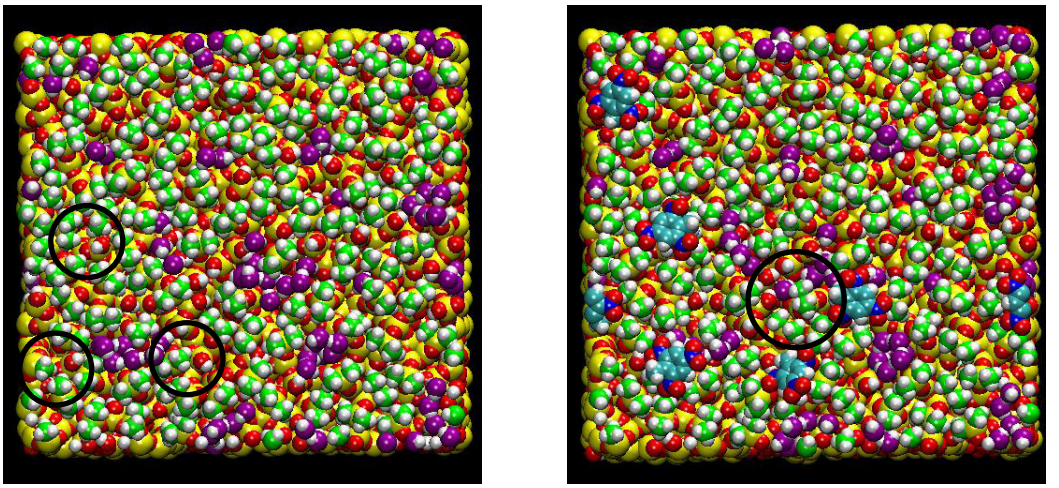


Fig. 4. Wet methylated silica surface alone (left) and with TNT adsorbed (right). Three TNT molecules appear to interact with the silanols enclosed on the left picture, while only the TNT molecule enclosed on the right picture clearly interacts with a water molecule.

5. Conclusions

Realistic models of silica surfaces with full atomistic resolution have been set up and validated against N_2 adsorption data. Additional experiments – including measurement of water isotherms at low pressure – could provide a more stringent validation of these surfaces. In future work, predictions of the mass uptake of various detection targets and pollutants that may be present in the atmosphere should contribute to the design of novel sensitive materials specifically optimized for the application in view.

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